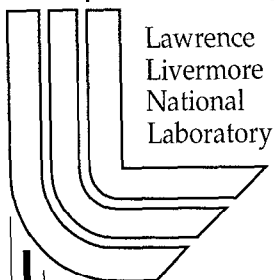


29th Annual PolyMAC Meeting: Book of Abstracts

B. Balazs

July 23, 1999

U.S. Department of Energy



Lawrence
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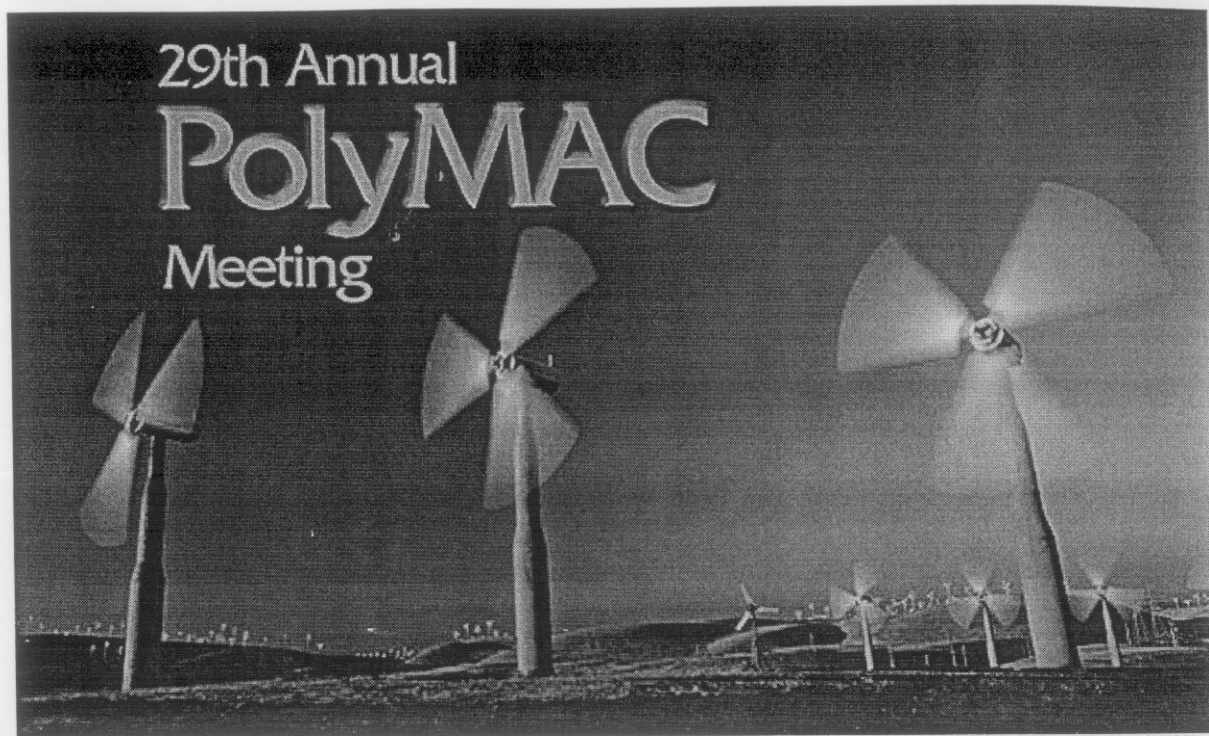


Photo courtesy of Scott Dougherty, LLNL

***29th Annual PolyMAC Meeting
(Polymers, Materials, Adhesives and Composites)***

**June 8–10, 1999
Lawrence Livermore National Laboratory
Livermore, CA 94550**

Book of Abstracts

UCRL-ID-134662

**Compiled by Bryan Balazs
Chemistry and Materials Science Directorate
Lawrence Livermore National Laboratory**

Lawrence Livermore National Laboratory is administered by the University of California for the U.S. Department of Energy under contract number W-7405-ENG-48.

PolyMAC Attendees



Acknowledgments

The hosts of this conference gratefully acknowledge the help of:

George Overturf

Jim LeMay

Helen Meredith

Leslie Spellman

...Thanks!

Agenda

TUESDAY—JUNE 8th

Morning Sessions

- | | |
|-------------|--|
| 8:30–9:00 | Badging & Refreshments |
| 9:00–9:30 | Welcome/Logistics |
| 9:30–10:00 | Site Overviews
KCP, LANL, LLNL, Oak Ridge/Y-12, Pantex, SNL, AWE |
| 10:00–10:45 | DP Campaigns (James LeMay) |
| 10:45–11:00 | BREAK |
| 11:00–12:00 | Adhesives, Bonded Joints & Coatings (Chair: John Emerson)
“Evaluation of Surface Pre-treatments of titanium alloy and (Polyether-ether-ketone) (PEEK) for adhesive bonding”, C J Allen and N R Godfrey (AWE)
“Adhesives for bonding aluminium and steel in trial assemblies”, J L McGrath and N R Godfrey (AWE) |
| 12:00–1:00 | LUNCH |

Afternoon Sessions

- | | |
|-----------|---|
| 1:00–3:15 | Adhesives, Bonded Joints & Coatings (Chair: John Emerson)
“Interactions Among Variables During Electrophoretic Deposition of an Acrylic Coating”, Robert Sanders (KCP)
“Thermal Characterization of the BT-Epoxy/Duroid Printed Wiring Board Laminate”, Rebecca Cohenour, James Lula, and Floyd Gentry (KCP/SNL-NM)
“Strength and fatigue life of epoxy bonded composite-to-steel tubular joints”, Mark E. Stavig (SNL-NM)
“Adhesive Evaluation & Procedures for Bonding High Density IC Assemblies for Satellite Applications”, David L. Zamora and John Emerson (SNL-NM) |
| 3:15–3:30 | BREAK |
| 3:30–5:00 | Pottings & Encapsulants (Chair: Bob Sanders)
“Development of Compliant Halthane Potting Compounds”, S. DeTeresa and L. Thompson (LLNL/Y-12)
“Removable Encapsulants for the W76 Upgrade: MC4081-2 Clocks Encapsulated with Removable Epoxy Syntactic Foam”, Edward M. Russick, James H. McElhanon, Patricia S. Sawyer, Sharlene F. McLane (SNL-NM)
“Non-bonding polymeric pottings for use in ultra dry environments”, C J Page, R K Scarrow and N R Godfrey (AWE)
“Flow Visualization Techniques for Improving Encapsulation Processes”, Howard W. Arris (SNL-CA)
“An Update on Formulated Replacements for EN-7 and Other Polyurethane Elastomers”, Linda Domeier and Pat Keifer (SNL-CA) |
| 6:30 | BBQ Social |

Agenda

WEDNESDAY—JUNE 9th

Morning Sessions

8:30–10:00

Polyurethanes (Chair: LeRoy Whinnery)

“Designed (Taguchi) experiments for the analysis of formulation and processing variables on the performance of polyurethane foams”, C J Lord, C J Page & N R Godfrey (AWE)

“Establishing a WR Qualification Test Matrix for Rigid Polyurethane Foams”, LeRoy Whinnery and Steve Goods (SNL-CA)

“The Effects of Thixotropic Nucleating Agents on Polyurethane Foam Encapsulants”, David J. Irvin, LeRoy L. Whinnery, and Steve H. Goods (SNL-CA)

“Polymer Production at the Kansas City Plant”, Tricia Wilson (KCP)

10:00–10:15

BREAK

10:15–12:00

Silicones I (Chair: David Spieker)

“Development Work on Silicone Vacuum Backfill”, Lisa Thompson (Y-12)

“Ageing and Characterisation of Polysiloxane rubbers”, M. Patel and A.R. Skinner (AWE)

“Mechanical Characterization and Stress Relaxation of Filled Silicone Foams - Understanding the Time Dependent Behavior of Strained Flexible Foams”, James Coons, Thomas Stephens, Alan Graham, Gary Gladysz, Rick Mooday, Warren Steckle, Micky Clifford, David Spieker, Lisa Thompson, and George Dorsey (LANL/KCP/Y-12)

12:00–1:00

LUNCH

1:00–1:15

PHOTO SHOOT

Afternoon Sessions

1:15–2:30

Silicones II (Chair: Lisa Thompson)

“Recent Silicone Cushion Analysis Results”, David Spieker (KCP)

“Desorption kinetics of H₂O, H₂, CO, and CO₂ from silicone”, Long Dinh and Mehdi Balooch (LLNL)

“Replacement Activities For Y-1587 Process Aid used in the Compounding of Cellular Silicone Materials”, Jim Schneider (KCP)

2:30–2:45

BREAK

2:45–5:00

Testing (Chair: Jim Coons)

“A Comparison of Linear Dynamic Mechanical Analyzers - Results of an InterLaboratory Study”, James Coons, Michael Clifford, Lisa Thompson, and George Dorsey (LANL/KCP/Y-12)

“A Comparison of Results from Linear and Rotational Dynamic Mechanical Analyzers,” Mickey Clifford (KCP)

“Contact Mechanics using the JKR Technique - A System Description”, Gregory V. Miller, John A. Emerson, and Raymond A. Pearson (SNL-NM)

“Self-Adhesion of a Model Siloxane Elastomer using the JKR Technique”, John A. Emerson, Gregory V. Miller, Christopher R. Sorensen, and Raymond A. Pearson (SNL-NM)

Agenda

THURSDAY—JUNE 10th

Morning Sessions

8:30–10:30

Damage, Aging & Degradation (Chair: Graeme Nicholson)

“Methods for characterisation of ageing mechanism in loaded rubber”, IM Horn, AR Skinner (AWE)

“Characterisation of degradation reactions in loaded rubber by pyrolysis GCMS”, IM Horn, AR Skinner (AWE)

“Measurement of Volatile Evolution Induced by Exposure to Simulated Radiation”, J. Murphy, M. Patel, S. Powell and P. Smith (AWE/LANL)

“Gamma radiation damage of filled silicones”, Allen Chien, Bryan Balazs, David Chambers, James LeMay (LLNL)

“NMR Characterization of Motional Properties of Siloxane Based Stress Cushions”, Robert Maxwell, Bryan Balazs, James LeMay (LLNL)

10:30–10:45

BREAK

10:45–11:30

Materials Substitutions & Replacements (Chair: Norm Godfrey)

“Solvent Substitution Wipe Study Update/Joint Study Between Sandia & Pantex”, Eddie Lopez, Ed Case, Bill Moddeman, Kevin Brown, Jerry Taylor, & Lorelei Woods, (SNL-NM/Pantex)

“Less toxic alternatives for the manufacture of polyurethane and syntactic foams”, D R Harbron, C J Page, R K Scarrow & N R Godfrey (AWE)

“Crystallinity in fluoropolymer binders for PBX's”, G. E. Overturf III, R. C. Cook, R. Weese, Cheng Saw, (LLNL) W. Rodin (Pantex)

11:30–1:00

LUNCH

Afternoon Sessions

1:00–2:00

JOWOG 28 Review (Chairs: Cliff Renschler/Norm Godfrey)

2:00–3:00

Cleaning & Contamination Control IMOG

PolyMAC '99 Attendees

Atomic Weapons Establishment (AWE)

Norman Godfrey	ngodfrey@awe.co.uk
Ian Horn	
Graeme Nicholson	gnicholson@awe.co.uk
Chris Page	

Allied Signal, Federal Manufacturing & Technologies (KCP)

Micky Clifford	mclifford@kcp.com
Rebecca Cohenour	rcohenour@kcp.com
George McEachen	gmceachen@kcp.com
Bob Sanders	bsanders@kcp.com
Jim Schneider	jschneider@kcp.com
David Spieker	dspieker@kcp.com
Tricia Wilson	tmwilson@kcp.com

Lawrence Livermore National Laboratory (LLNL)

Bryan Balazs	balazs1@llnl.gov
Mehdi Balooch	balooch1@llnl.gov
Allen Chien	chien1@llnl.gov
Charles Chow	chow4@llnl.gov
Anthony DePiero	depiero1@llnl.gov
Steve DeTeresa	deteresa@llnl.gov
Long Dinh	dinh1@llnl.gov
Weldon Hall	hall32@llnl.gov
Pat Harwood	harwood3@llnl.gov
Mark Hoffman	hoffman2@llnl.gov
John Kolb	kolb1@llnl.gov
Jim LeMay	lemay1@llnl.gov
Patricia Lewis	lewis20@llnl.gov
Robert Maxwell	maxwell7@llnl.gov
George Overturf	overturf1@llnl.gov
Wigbert Siekhaus	siekhaus1@llnl.gov
Andreas Toupadakis	toupadakis@llnl.gov
Randall Weese	weese2@llnl.gov

Los Alamos National Laboratory (LANL)

Fred Bryant	bryant@lanl.gov
Jim Coons	jimc@lanl.gov
Luke Ney	Luke@lanl.gov

Mason & Hangar Corporation (Pantex)

Kevin Brown	kbrown@pantex.com
Jerry Taylor	jdtaylor@pantex.com

Sandia National Laboratory (SNL-CA)

Linda Domeier	domei@sandia.gov
Steve Goods	shgoods@sandia.gov
David Irvin	djirvin@sandia.gov
Jennifer Irvin	jairvin@sandia.gov
Bernice Mills	mills@sandia.gov
Carl Pretzel	cwpretz@sandia.gov
Dawn Skala	dmsabel@sandia.gov
LeRoy Whinnery	llwhinn@sandia.gov

Sandia National Laboratory (SNL-NM)

Howard Arris	hwarris@sandia.gov
Jim Aubert	jhauber@sandia.gov
John Emerson	jaemers@sandia.gov
Eddie Lopez	eplopez@sandia.gov
Greg Miller	gvmille@sandia.gov
Cliff Renschler	clrensc@sandia.gov
Ed Russick	emrussi@sandia.gov
Mark Stavig	mestavi@sandia.gov
Dave Zamora	dlzamora@sandia.gov

Oak Ridge National Laboratory (Y-12)

Lisa Thompson	tpn@ornl.gov
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Evaluation of Surface Pre-treatments of Titanium Alloy and (Polyether-ether-ketone) (PEEK) for Adhesive Bonding

C. J. Allen and N. R. Godfrey (AWE)

Adhesives for Bonding Aluminium and Steel in Trial Assemblies

J. L. McGrath and N. R. Godfrey (AWE)

Interactions Among Variables During Electrophoretic Deposition of An Acrylic Coating

Robert S. Sanders, AlliedSignal Inc., Federal Manufacturing & Technologies

A sixteen-run, Resolution IV, fractional factorial screening design has been used to evaluate the relative significance of seven independent material and process variables for an electrically deposited commercial acrylic paint. A Resolution IV design was chosen so that variable interactions could be detected without any interference from the effects of the variables themselves. Because resource limitations did not permit use of a Resolution V design, the two-way interactions were confounded with one another in groups of three, which unfortunately made interpretation of the results more complicated. Each design point was replicated once and a pair of centerpoints were run at the beginning, in the middle and at the end of the design points. A total of 38 test panels were prepared. Independent variables used in this experiment were total charge, current density, mixer speed, silica content, crossover point, temperature and solids fraction.

The magnitude of each independent variable's effect on the dependent response variables was estimated by fitting a first-order model with two-way interaction terms. Three-way interactions were assumed to be insignificant. Interaction confounding was eliminated by using the significance of the independent variables to determine which of the three possible interactions was significant. Data analysis was performed using the Bayes Plot option of the JMP statistics program from SAS Institute. Only effects with a posterior probability equal to or greater than 0.95 were considered to be significant. Response variables analyzed were weight deposited, film thickness, surface roughness and plating efficiency. Results of the analysis are summarized in Table 1.

Table 1. Data Analysis Summary

Variable	Significant Effect for One or More Response Variable?	Significant Interaction with One or More Independent Variable?
Total Charge	Yes	Yes
Current Density	Yes	Yes
Mixer Speed	Yes	Yes
Silica Content	Yes	Yes
Crossover Point	Yes	No
Temperature	No	No
Solids Fraction	No	No

The following conclusions were formulated from the analysis of this experiment:

- Centerpoint behavior brings shelf-stability of the aqueous paint baths into question.
- Interactions among the material and process variables are present and significant.
- The magnitudes of some interaction effects equal or exceed the magnitudes of some of the effects of the independent variables.
- Silica is detrimental to surface smoothness, interacts strongly with other variables, is hard to keep suspended in aqueous baths, and should be replaced with a liquid rheology control agent.
- Because of the significance of two-way variable interactions, One-Variable-At-A-Time experiments with this material and process could lead to erroneous conclusions about variable effects.

Thermal Mechanical Characterization of a BT/Duroid PWB Laminate

Rebecca Cohenour, AlliedSignal FM&T, rcohenour@kcp.com, (816) 997-2793,

James Lula, AlliedSignal FM&T, jlula@kcp.com, (816) 997-2417,

Floyd Gentry, SNLA, flgentr@sandia.gov, (505) 845-9202

Thermal Mechanical Analysis (TMA) of a printed wiring board (PWB) provides information about laminate performance during temperature changes. This information is useful to predict problems that may occur during component soldering as the PWB laminate is subjected to temperatures of 500°F or more. The information can also predict problems that may occur during normal environmental temperature cycling while the PWB assembly is in stockpile or in use. Typical environmental temperature cycles may range from -65°C to +125°C, and while mild compared to the initial soldering temperatures, repetitive temperature cycling in this range will eventually fatigue the copper plating and solder joints. Cracks in the copper plating and solder joints decrease the electrical reliability.

TMA yields the thermal expansion characteristics of the PWB substrate, glass transition temperature (T_g) of the polymer resins, and delamination resistance of the laminate at elevated temperatures such as occur during soldering operations. Taken as a whole, these parameters are useful in characterizing new laminate systems and comparing them to PWB laminate materials already in WR applications.

TMA was used to evaluate a new composite PWB assembly of BT Epoxy/glass and Duroid and the results were compared to type GF and type GI laminated PWBs already in WR applications. While thermal expansion and glass transition data is within typical bounds, test results indicated that several test specimens were prone to delaminations above 250°C, or within the soldering temperature range. It was recommended that a review of the PWB lamination process be conducted, specifically focusing on prepreg drying, inner layer bakeout, cure cycle and copper foil oxide surface treatments.

Strength and Fatigue Life of Epoxy Bonded Composite-to-Steel Tubular Joints*

*M. E. Stavig, T. R. Guess and K. E. Metzinger, Sandia National Laboratories
Albuquerque, New Mexico 87185*

Sandia has an experimental/analytical program to study issues related to the strength and fatigue life of composite-to-steel tubular joints of the type found in wind turbine blades. In these blades, the composite airfoil is epoxy bonded to a metallic hub. Failure of these bonded joints appears to initiate at the epoxy/metal hub interface. In this presentation, we will describe an experimental study in which generic, tubular, composite-to-steel joints are subjected to tension and compression loading in both single-cycle and cyclic fatigue tests. Specimens with non-tapered and tapered steel adherends are used to assess the effects of peel stresses on the strength and lifetime durability of bonded joints. Compressive and tensile axial loads of the same magnitude produce stresses in the epoxy bonding material with very similar magnitudes but opposite signs. (For the joints considered, tensile loads produce compressive peel stresses in the adhesive at the location where debonding initiates.) The tensile specimens failed at much higher loads, establishing that the sign of the adhesive peel stresses are also critical for fatigue loading. Results of low-cycle, axial fatigue tests are presented. In addition, test results are complemented with finite element analyses that demonstrate the localized nature of the peel stresses that develop at the failure initiation site.

*Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract No. DE-AC04-94AL85000.

Adhesive Evaluation & Procedures for Bonding High-Density IC Assemblies for Satellite Applications

*David L. Zamora and John A. Emerson Sandia National Laboratories,
Albuquerque, NM 87185*

In a joint effort with Boeing North America, Sandia has been tasked to develop high-performance satellite hardware. As materials consultants for the assembly of high-density circuits, we have been selecting/evaluating adhesives and developing processes in areas of die attachment, underfill technology and the stacking of ceramic chip carriers. This presentation will discuss the material choices and processes required in building these complex electronic assemblies.

Development of Compliant Halthane Potting Compounds

S. J DeTeresa and W. H. Siegel (LLNL), and L. M. Thompson (ORNL/Y-12)

The use of flexible polymeric microspheres to increase the volumetric compliance of Halthane adhesives and potting compounds was investigated. Low-pressure compressibility measurements were used to examine the response of both Halthane 73-18 and 88-3 polyurethanes having a range of filler concentrations. The relative increase in compressibility of the two urethanes loaded to similar filler concentrations was found to be significantly different. This difference was attributed to the dissimilar shear moduli of the base polymers. The volume strain require to achieve full compaction was confirmed to be simply related to the volume fraction of microspheres. Once compressed to these high levels, the materials exhibited a time-dependent compression "set" that took days to partially recover at ambient conditions. However, below these compression levels, the filled materials appeared to behave elastically. The shear strengths of Halthane 73-18 filled with 32 vol.% microspheres and bonded to several materials were found to be better than the strengths of bonds made using solid APC-2.5 silicone. Measured shear moduli and coefficients of thermal expansion, as well as microscopic examination of tensile fracture surfaces all indicated that the microspheres adhered well to the Halthane 73-18 matrix. However, it may be desirable in some applications to treat the surface of the microspheres to eliminate this bond.

Removable Encapsulants for the W76 Upgrade: MC4081-2 Clocks Encapsulated with Removable Epoxy Syntactic Foam*

*Edward M. Russick, James R. McElhanon, Patricia S. Sawyer, Sharlene F. McLane,
Encapsulants and Foams Department,
Sandia National Laboratories, Albuquerque, NM 87185*

Removable encapsulants that can be easily and selectively removed to repair, replace, and upgrade components for weapon stockpile life extension have long been desired in the DOE weapons complex. We are developing removable encapsulants based on Diels-Alder reversible chemistry that are stable at normal operating conditions but dissolve in n-butanol at 90°C to allow for depotting of repairable components. MC4081-2 clock circuits were encapsulated in removable epoxy syntactic foam, thermally cycled, and depotted with electrical testing performed before and after potting, during thermal cycling, and after depotting. The encapsulation experiments were done to determine if application of the removable syntactic foam, thermal cycling, and encapsulant removal damages or causes malfunctioning of the clock circuits. MC4081-2 clocks were chosen for these experiments because they have proven to be troublesome when potted and thermally cycled with other conventional encapsulants. Results of the encapsulation experiments including processing, thermal cycling conditions and electrical testing results will be presented. The chemical mechanism employed in the removable epoxy encapsulant will be discussed. Initial results of an accelerated aging study on the removable epoxy syntactic foam will also be discussed.

Non-bonding Polymeric Pottings for use in Ultra Dry Environments

C. J. Page, R. K. Scarrow and N. R. Godfrey (AWE)

Flow Visualization Techniques for Improving Encapsulation Processes

*Howard W. Arris, Organic Materials Department, Sandia National Laboratories**

The ability of weapons component assemblies to survive environmental conditions such as shock, vibration and thermal cycling is often dependent on the appropriate use of polymeric encapsulating materials. Encapsulants also provide electrical components high voltage protection and isolation. These systems are designed specifically to meet the needs of the component and include consideration of component lifetime, operating conditions, shock and thermal exposure.

The encapsulation process for the MC4368 neutron generator is a “dual pour” encapsulation process. Two different encapsulants are poured in series while in a liquid state. The first encapsulant is an alumina filled Epon 828 epoxy, aromatic amine cured, and is intended to stand off high voltage in the power supply and transmit shock from the timer driver to the ferroelectric ceramic power supply. The second encapsulant, a rubber modified epoxy, filled with high compressive strength glass microballoons (GMB) and amine cured, is intended to provide high voltage stand off and shock mitigating properties to the tube.

Historically, the encapsulating process consisted of a gravity fill at atmospheric pressure for the alumina-filled epoxy around the power supply, and a vacuum pour of the GMB epoxy through the top sprue of the neutron generator mold. The MC4368 neutron generator utilized this type of pour process in the development stages. Voids in the GMB encapsulant proved to be a continuous problem, resulting in high voltage breakdown (HVB) failures.

Model Accreditation Via Experimental Sciences for Nuclear Weapons (MAVEN) funded the development of flow visualization equipment and studies to analyze the flow properties of filled polymer systems. The neutron generator production process is a mission critical Sandia program, and flow visualization was utilized to try and understand void entrapment in the MC4368. Production neutron generator molds were modified to enable flow visualization during the “dual pour” process. Flow visualization demonstrated that the “top pour” process was responsible for void entrapment around the neutron tube. The epoxy effectively blocked trapped air release. Sandia process engineers developed a “new” side pour process where the GMB epoxy is injected through the alumina epoxy side pour sprue. Large voids within the cured encapsulant and surface voids on the finished parts have been eliminated resulting in fewer scrapped parts and reduced re-work costs.

An overview of the MC4368 neutron generator flow visualization techniques, flow visualization of the MC4368, and the resultant “new” side pour process, including a short video of the encapsulation process along with still images captured from the video, will be presented.

*This work was performed at Sandia National Laboratories, which is supported by the United States Department of Energy under contract number DE-AC04-94AL8500. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy.

An Update on Formulated Replacements for EN-7 and Other Polyurethane Elastomers

*Linda Domeier and Pat Keifer, Sandia National Laboratories
Livermore, California*

Versatile and easily processed replacements are needed for EN-7, a polyurethane potting elastomer containing undesirable levels of OSHA regulated TDI (toluene diisocyanate). A simple formulation approach to such materials has been investigated which avoids the need for prepolymer synthesis and which provides a family of products suitable for different performance and processing requirements. Various commercial liquid diisocyanates were mixed with appropriate levels of polybutadiene diol plus low molecular weight polyol cross-linkers and ferric acac. Most formulations used the EN-7 Part B cross-linker which provides a convenient premix of catalyst and polyols. The low viscosity mixed formulations are simply degassed, poured and cured. Pot-lives and general processability have been as good or better than EN-7.

Several formulations gave good performance profiles with both electrical and mechanical performance similar to EN-7. One, DK-502, is recommended as a replacement material. Formulation details and test data will be provided.

Designed (Taguchi) Experiments for the Analysis of Formulation and Processing Variables on the Performance of Polyurethane Foams

C. J. Lord, C. J. Page and N. R. Godfrey (AWE)

Establishing a "WR Qualification" Test Matrix for Rigid Polyurethane Foams

LeRoy Whinnery and Steve Goods, Sandia National Laboratories, Livermore, CA

Over the past several years, we have developed a replacement foam (RE-CRETE) for TDI containing rigid, water-blown polyurethane foams. Our replacement foam has been formulated to match the processing (e.g., rise time, gel time and maximum temperature) and mechanical properties (e.g., collapse stress and modulus) of the TDI containing foams. In addition, RE-CRETE uses a polyether polyol, instead of a polyester polyol, for increased hydrolytic stability. Also, its formulation uses a non-migratory catalyst that should help minimize volatiles.

Unfortunately, there is no standard methodology or series of tests established to allow a new material to be approved for use in a weapon system. The only actual requirements are to write a quality acceptance specification and to obtain a specification number from ASFM&T. After meeting these criteria, the material can be used in a weapon. There are, in fact no additional requirements to either document the performance characteristics of the materials or even to show that it will do no harm to the remainder of the system (outgassing, for example).

Our proposed test matrix involves the characterization of both zero-aged foams and laboratory-aged foams. Zero-aged testing focussed on mechanical properties (compression, tension, impact, rate and temperature effects), but will also include electrical properties (dielectric constant and volume resistivity). Laboratory aging will again be focussed on mechanical properties (compression, tension, impact). This data, however, will be correlated to DMA/TMA (T_g) measurements. Such measurements are often used as an indication of aging induced changes, but cannot be specifically correlated to mechanical performance. Favorable results have been obtained from preliminary outgassing studies of RE-CRETE foams.

The Effects of Thixotropic Nucleating Agents on Polyurethane Foam Encapsulants

David Irvin, LeRoy Whinnery, and Steve Goods, Sandia National Laboratory, Livermore, CA

Sandia has long used polyurethane and other foam encapsulants for a wide range of functions including vibration and shock dampening, space filling, and obscurant barrier. The stability and reliability of these foams is an issue of the utmost importance. With the micro-capacitive discharge unit (CDU) and other high voltage components shrinking in scale there is increased concern over high voltage breakdown. Currently, glass microballoon (GMB) filled epoxy is used in high voltage applications. Polyurethane foams have a few advantages over the GMB filled epoxy: lower density, more easily processed, and lower heat transfer. The disadvantage of polyurethane foams is comparatively large cell size.

Working under the assumption that lower average cell size and the smallest maximum cell size leads to an increased voltage breakdown strength. Our approach to increasing the high voltage breakdown (HVB) strength of polyurethane foams is to decrease the cell size to preferably $\sim 100 \mu\text{m}$. We have examined chemical parameters to reduce average cell size including catalysts and surfactants. The purpose of changing the catalyst is to increase the viscosity before and during gas generation to decrease cell coalescence. Surfactants were used to tune surface energy of the forming cells. An additional approach to decrease the cell size was to induce the formation of a greater number of cells by the incorporation of nucleating agents. We have also varied processing parameter such as mixing speed and type of mix head to improve the cell size. A method for the rapid quantification of cell size and distribution was developed to aid in our research.

In conclusion, with improvements in mixing, we are able to produce uniform foams. We found that the chemical influences were small, but still had a significant effect on the cell size and distribution. We also found that nucleating agents had a much smaller effect on the cell size than processing, catalysts or surfactants, and significantly decreased the mechanical strength of the foams.

Polymer Production Facility Capabilities Update

Tricia Wilson, AlliedSignal Federal Manufacturing & Technologies
Kansas City, Missouri*

The Kansas City Plant's Polymer Production Facility has historically both synthesized and manufactured specialty polymeric materials for use within the Weapons Complex. Process enhancements are an important part of the manufacturing process. This traditional work continues along with other innovative processes. One such innovative process involves the recovery of R-12, a chlorfluorocarbon, from a highly viscous hydrocarbon resin. The separation process was a technical challenge due to the unique nature of the material. The success of this process recovered over 30,000 pounds of R-12 and netted the customer \$150K from the sales of the R-12.

*Operated for the United States Department of Energy under Contract Number DE-AC04-76-DP00613.

Development Work on Silicone Vacuum Backfill

Lisa Thompson (Y-12)

Ageing and Characterisation of Polysiloxane Rubbers

M. Patel and A.R. Skinner (AWE)

Mechanical Characterization and Stress Relaxation of Filled Silicone Foams

Understanding the Time Dependent Behavior of Strained Flexible Foams

*James Coons, Thomas Stephens, Alan Graham, Gary Gladysz, Rick Mooday,
Warren Steckle, Los Alamos National Laboratory, Los Alamos, New Mexico*

*Micky Clifford and David Spieker, AlliedSignal-Federal Manufacturing and Technology,
Kansas City, Missouri*

*Lisa Thompson and George Dorsey, Oak Ridge Y-12 Plant
Oak Ridge, Tennessee*

The objective of this investigation is to predict the long-term stress relaxation in foams in which the continuous phase is polysiloxane polymer reinforced with solid fillers. Obtaining high accuracy, reproducible mechanical test data in these systems presents special challenges that will be described. Rusch¹ showed in the late sixties that the response of several flexible polymeric foam materials undergoing compression can be described by the product of an elastic modulus and an empirically determined strain function. The foams are highly nonlinear under compression and a method is developed to estimate the linear compressive modulus. Meinecke and Clark² later reported that the stress relaxation behavior of many flexible foams is well described by a time and temperature-dependent relaxation modulus and a strain dependent shift factor. Instrument artifacts limit the duration of the relaxation experiments to less than 100 seconds. In this paper, concepts from both of these works are used to develop a constitutive model for a commercially available silica-filled PDMS foam. This constitutive equation combines the elastic moduli and short duration (10 second) stress relaxation of the material to predict long-term stress relaxation in these foams. Model predictions are compared to data collected in a 2 year independent study. Physical relaxation is shown to result in significant changes in compressive stress but may not control the stress decay over long times.

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1. K. C. Rusch, *J. Appl. Polym. Sci.*, 1969, 13, 2297.
 2. E. A. Meinecke and R. C. Clark, *Mechanical Properties of Polymeric Foams*, 1973, Westport, Conn: TECHNOMIC Publishing Co., Inc.

Recent Silicone Cushion Analysis Results

David A. Spieker, AlliedSignal Federal Manufacturing & Technologies
Kansas City, Missouri*

Crosslinked poly(dimethylsiloxane) (PDMS) elastomeric foams are used to manufacture silicone cushions for NWC applications. On a time scale of several years, the load retention properties of these materials decrease with time. The physical phenomena that give rise to this decrease in load retention properties are not well understood.

Crosslink density as a function of part age is assumed to be an important parameter in understanding time dependent load retention behavior. Solvent swell is the method of choice for studying crosslink density, but is difficult to apply to foamed elastomers for two reasons. First, solvent swell measurements yield artificially high gravimetric data due to entrapment of swelling solvent in the foam cells. Second, the fumed silica reinforcing filler in the product hydrogen bonds at various sites along the PDMS chain, artificially increasing the apparent crosslink density.

A solvent swell technique is being developed to obviate both of these complications. The method is a modification of a literature method that was applied to full density reinforced PDMS elastomers.¹ The procedure involves swelling the samples over toluene in a room temperature desiccator, then placing beakers containing concentrated ammonium hydroxide in the desiccator. Ammonia evaporates into the desiccator headspace and diffuses into the polymer to effect breakage of the hydrogen bonds. This presentation will describe the technique and present results generated using it.

¹Vondracek and M. Schatz, NH₃-Modified Swelling of Silica-Filled Silicone Rubber, *J. Appl. Polym. Sci.*, **23**, 2681-2694 (1979)

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Desorption Kinetics of H₂O, H₂, CO, and CO₂ from Silica Reinforced Polysiloxane

*L. N. Dinh, M. Balooch, Chemistry and Materials Science Directorate
Lawrence Livermore National Laboratory, Livermore, CA*

We performed temperature programmed desorption up to 500K on silica-reinforced polysiloxane in both solid and foamed forms (M9787 and M9750 respectively). Our data show that H₂O was the dominant desorbing species in both forms of silicone (on the order of 100 µg of water per gram of polymer), which are expected to be very hydrophilic when dehydrated. Detailed studies of the TPD spectra of H₂O from the silicones and from the fumed silica fillers suggest that H₂O molecules preferentially adsorbed on the surface of silica particles contained in the silicones with activation energies of desorption of 15 ± 3 kcal/mol and 50 ± 10 kcal/mol. There was strong evidence of H₂ desorption below 400 K from the silicones. The equivalent concentration of H₂ in the silicones was 0.44 µg of H₂ per gram of silicone. Other species desorbing from the silicones were CO, and CO₂ with concentrations on the order of 2.5 µg, and 1.6 µg per gram of silicone and activation energies of desorption of 10 ± 2 kcal/mol and 9.5 ± 1.5 kcal/mol, respectively.

Replacement Activities for Y-1587 Process Aid used in the Compounding of Cellular Silicone Materials

Jim Schneider, AlliedSignal Federal Manufacturing & Technologies
Kansas City, Missouri*

The Y-1587 process aid, Union Carbide Corporation (UCC) ethoxy endblocked polydimethylsiloxane fluid, is used in the compounding of silica reinforced M-97 silicone polymers. Currently, the W87 and B-61 are the main users of cellular silicone material based on the M-97 formulation. In the past, the Y-1587 was also used with the RG-97 and W-97 silicone polymers.

OSi-Witco, the current owner of the silicone division of UCC, has deemed this material obsolete and will no longer produce it. AlliedSignal has approximately a ten month supply of unlimited shelf life of Y-1587 to cover production requirements.

This presentation will cover the replacement activities to date that are on going with NuSil Technology to develop an acceptable replacement material.

Comparison of Linear and Rotational Dynamic Mechanical Analyzers

Micky Clifford (KCP) and Jim Coons (LANL)

A round robin of testing was performed to compare the performance of dynamic mechanical analyzers (DMAs) being used within the nuclear weapons complex. Analysis is regularly performed at the different sites, but no standard exists to validate the comparison of results. Principals from Sandia National Laboratories, New Mexico; Lockheed Martin Y-12 Plant at Oak Ridge, Tennessee; Los Alamos National Laboratory, New Mexico; and AlliedSignal FM&T, Kansas City, MO; performed identical testing of hydrogen blown polysiloxane S-5370 and the elastomer J-Rubber on linear DMAs and testing on S-5370 and bisphenol polycarbonate on rotational DMAs. Compatibility of results varied from test to test. The ability to replicate the testing parameters and conditions determined the success of the tests.

Contact Mechanics using the JKR Technique— A System Description

Gregory V. Miller, John A. Emerson, and Raymond A. Pearson (SNL-NM)

Work of adhesion, W_a , measurements are being studied for numerous types of polymer/metal combinations to better understand the adhesive failure mechanisms for encapsulated and bonded components systems. The principal concern is whether studies of model systems can be extended to systems of technical interest. Samples based on vinyl-capped poly (dimethylsiloxane) mixed with tetrakis (dimethylsiloxy) silane in the presence of platinum catalyst to form a cross-linked poly (dimethylsiloxy) (PDMS) were used to measure the Work of Adhesion, W_a . A contact mechanics method – JKR uses two contacting hemispheres to determine the W_a . Silicone networks were examined as synthesized, as extracted with toluene and/or reacted with ethylene. The JKR technique has been automated allowing the testing of sample polymers by means of user defined parameters. This includes loading and unloading intervals, maximum loading, image analysis, and data acquisition. The advantages of automation include electronic timing and precision, hands-off testing and ease of use. Details about the basic JKR technique, the automated apparatus, and the material synthesis will be discussed in this presentation.

Self-Adhesion of a Model Siloxane Elastomer using the JKR Technique*

*John A. Emerson, Gregory V. Miller, Christopher R. Sorensen, and
Raymond A. Pearson[†], Sandia National Laboratories, Department of Organic Materials
Albuquerque, Nm 87185-0958*

Samples based on vinyl-capped poly(dimethylsiloxane) mixed with tetrakis(dimethylsiloxy) silane in the presence of a platinum catalyst to form a cross-linked poly(dimethylsiloxane) (PDMS) were used to study the self-adhesion hysteresis. A contact mechanics method – JKR method using two hemispheres – was deployed to measure the degree of hysteresis. Silicone networks were examined as synthesized, extracted with toluene and/or reacted with ethylene. No hysteresis (loading and unloading) is observed with as synthesized PDMS that has been post-cured. However, hysteresis is always observed after toluene extraction. Factors effecting the degree of hysteresis were examined from surface texture changes, free hydride, and the effects of processing.

Self-adhesion hysteresis has been observed for a number of treated PDMS hemispheres. The presence of Si-H groups is not required for hysteresis. Therefore, it is likely that hysteresis is due to the presence of tethered chains that entangle prior to unloading.

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[†] On sabbatical leave from Lehigh University

Methods for Characterisation of Ageing Mechanism in Loaded Rubber

I. M. Horn, A.R. Skinner (AWE)

Characterisation of Degradation Reactions in Loaded Rubber by Pyrolysis GCMS

I. M. Horn, A.R. Skinner (AWE)

Measurement of Volatile Evolution Induced by Exposure to Simulated α Radiation

J. Murphy, M. Patel, S. Powell and P. Smith (AWE/LANL)

Gamma Radiation Damage of Cellular Silicones

*Allen Chien, Bryan Balazs, David Chambers, Robert Maxwell,
and James Le May, Lawrence Livermore National Laboratory, Livermore, CA 94551*

The effects of gamma radiation on the crosslink density of M97-series silica-reinforced silicone materials were investigated by solvent swelling. A two-step immersion swelling process was developed to measure crosslink density and isolate the contributions between the matrix polymer and the hydrogen bonded polymer/filler interface. Toluene is initially used to swell the polydimethylsiloxane (PDMS) polymer matrix; ammonium hydroxide is then added to break the hydrogen bonding at the polymer/filler interface. Swelling results show that for both solid and foam samples, the overall molecular weight between crosslinks (MW_x) initially increases (0-10 Mrad), indicating that the material becomes softer. At higher doses (<10Mrads), the material becomes gradually stiffer as shown by the decrease in MW_x . Our results also show that the initial softening is mostly due to a reduction of hydrogen bonding at the polymer/filler interface rather than bond scissioning within the matrix polymer. Lot-to-lot variations will also be discussed.

The environment in which the irradiation was performed shows a strong effect on the crosslink density of the polymer matrix. Samples irradiated in 1 mtorr of air vs. 1 atmosphere of air showed increased stiffness at lower doses. Gas chromatography/mass spectrometry (GC/MS) analysis of the volatile species produced in different environments as a result of irradiation shows high levels of toluene, benzene, and other degradation products are being created. NMR investigations of T_2 spin-spin relaxation time vs. dose corroborates the swelling results, which shows an initial softening; followed by a gradual stiffening of the polymer composite.

NMR Characterization of Motional Properties of Siloxane Based Stress Cushions

Robert S. Maxwell, Bryan Balazs, Allen Chien, James LeMay (LLNL)

There is a fundamental need to develop and employ spectroscopic methods to investigate the structural and motional changes that occur in organic materials as a result of aging in chemically, thermally, or radioactively harsh environments. Solid state NMR methods have demonstrated great ability to understand complex structural and motional processes occurring in a wide range of organic and inorganic polymeric systems. We have applied Nuclear Magnetic Resonance (NMR) methods to gain insight into the processes that are contributing to mechanical property changes as a consequence of aging in silica filled silicone cushions. The studies so far have concentrated on (A) Magic Angle Spinning (MAS) measurements of chemical speciation and (B) relaxation measurements to gain insight into molecular motional properties of the polymers.

The PDMS based polymers studied have three conveniently NMR observable nuclei: ^{13}C , ^{29}Si , and ^1H . NMR spectra of all three nuclei are potentially information rich and can provide detailed, quantitative chemical speciation from measurements of chemical shifts. In fact, MAS NMR spectra for virgin, stockpile return, and γ -irradiated samples reveal resonances that can be assigned to all but the vinyl species present in these materials; however, the MAS results presented failed to detect any speciation changes occurring via degradation mechanisms identified by GCMS studies.

In an effort to indirectly detect chemical changes via their effect on the molecular motional dynamics we have performed ^1H T_1 , T_2 , $T_{1\rho}$ and ^{29}Si $T_{1\rho}$ measurements under both static and MAS conditions and at 7T and 11.4T on a series of γ -irradiated, filled silicone stress cushions. ^1H T_1 measurements showed no difference, within experimental error, between virgin and irradiated samples at room temperature. However, as the temperature was increased, small differences were observed, suggesting that the energy of activation for rapid motional processes may be changing upon irradiation. ^1H T_2 measurements showed an initial increase in T_2 upon irradiation up to $\sim 5\text{Mrad}$ followed by a rapid decrease at higher doses. ^1H $T_{1\rho}$ relaxation times showed an initial small increase upon irradiation at 0.5Mrad followed by a gradual decrease as irradiation is increased to 50Mrad .

^{29}Si CP/MAS spectra are characterized by resonances broader than their MAS equivalents with additional broad resonances attributable to the silica filler, the sections of the PDMS chains directly hydrogen bonded to the silica filler, and the PDMS chains sections near hydrogen bonded sections. ^{29}Si $T_{1\rho}$ relaxation times for virgin and stockpile return samples were found to differ by an order of magnitude when measured by pulse-sequences employing CP preparation of the ^{29}Si spins.

Our preliminary results suggest that the measurement of relaxation times show great promise in characterizing the structural and dynamic processes that are changing upon irradiation, oxidation, mechanical stress, and/or time. The results reported here support conclusions from toluene and toluene/ammonia swelling experiments that suggest that irradiation initially causes a decrease in the interaction between the polymer network and the silica filler followed by gradual increases in the cross-link density in the polymer network. It is suggested that ^1H T_2 measurements can be calibrated (empirically and by correlation to molecular dynamics computational studies) to cross-link density and offer a non-destructive spectroscopic diagnostic tool for addressing aging related changes in silicone mechanical properties. Further development of CP methods are suggested for investigation of changes occurring at the polymer/filler interface.

***Solvent Substitution Wipe Study Update/Joint Study Between Sandia & Pantex**

E. P. Lopez, R. E. Case, Sandia National Laboratories, Albuquerque, NM

*W. E. Moddeman, K. Brown, J. Taylor, L. Woods, Pantex Plant,
Mason & Hangar Corporation, Amarillo, TX*

As part of a pollution prevention program, a study was conducted at Sandia National Laboratories and at the Amarillo, "Pantex Plant" to identify a suitable replacement solvent(s) for cleaning hardware during routine maintenance operations. Current cleaning is performed with solvents (e.g., acetone, toluene, MEK, isopropyl alcohol) that are classified as Resource Conservation and Recovery Act (RCRA) materials. The Environmental Protection Agency (EPA) has assigned four characteristics as the criteria for determining whether a material is identified as hazardous under RCRA: ignitability, corrosivity, reactivity and toxicity. Within the DOE and DoD sector, these solvents are used with hand wipes to clean surfaces prior to O-ring replacement, to remove decals for new labeling, to clean painted surfaces prior to reconditioning, and for other general maintenance purposes. In some cases, low-level radioactive contamination during cleaning necessitates that the RCRA solvent-containing wipes be classified as mixed waste. Mixed waste is generally very expensive and/or virtually impossible to dispose of. To avoid using RCRA materials, cleaning candidates were sought that have a flashpoint greater than 140°F, a pH between 2.5 and 12.5, and do not fail the reactivity and toxicity criteria. Three brominated cleaners, two hydrofluoroether azeotropes and two aliphatic hydrocarbon cleaner formulations were studied as potential replacements. Cleaning efficacy, materials compatibility of organic materials, compatibility with explosive materials, cure inhibition tests of adhesives and potting compounds, non-volatile residue studies of cleaner formulations, corrosion of metal alloys, accelerated aging studies and ES&H issues were conducted and used to screen potential candidates. Hypersolve NPB (an n-propyl bromide-based formulation) consistently ranked high in removing typical contaminants for weapons applications. The results of the study are presented.

*Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

Less Toxic Alternatives for the Manufacture of Polyurethane and Syntactic Foams

D. R. Harbron, C. J. Page, R. K. Scarrow and N. R. Godfrey (AWE)

Crystallinity in Fluoropolymer Binders for PBX's

G. E. Overturf III, R. C. Cook, R. Weese, Cheng Saw, (LLNL) W. Rodin (Pantex)

“Methods for characterisation of ageing mechanism in loaded rubber”

IM Horn, AR Skinner (AWE)

Loaded Rubber components fabricated from a mixture of neoprene and chlorobutyl rubbers have exhibited a small but significant increase in tensile strength with age when used in a system environment. AWE has undertaken a study to further characterise degradation mechanisms which will account for this observation. The samples under investigation have been aged thermally in both inert and oxidative environments and analysed using a variety of techniques. These techniques have also been used to assess real-time aged samples from a system environment. Preliminary results from these investigations suggest the presence of two mechanisms of degradation produced by thermal and radiation effects.

“Ageing and Characterisation of Polysiloxane rubbers”
M. Patel and A.R. Skinner (AWE)

Cured RTV 5370 siloxane rubbers have been thermally aged in an inert gas atmosphere in sealed containers at temperatures up to 80 °C. In a separate experiment, samples of rubber were aged in the presence of water ('hydrolysed') at 190 °C for 48 hours both in an sealed inert gas atmosphere and also open to the air.

Techniques used to probe the samples included mechanical testing, IRHD rubber hardness measurements, thermogravimetry (TGA), Differential Scanning Calorimetry (DSC), ATR infrared spectroscopy, toluene extractable matter and GC-MS of the toluene extractable fraction.

Mechanical and hardness measurements on samples thermally aged in a sealed inert environment indicated increased softening of the rubber. The TGA and toluene extractable matter measurements on these samples showed a build-up of low molecular weight fragments in the rubber network with age. Following toluene extraction, the mechanical & hardness data on the samples 'hydrolysed' in a sealed inert gas environment showed no significant change suggesting that the low molecular weight fragments in the rubber network (which increase with age) are not acting as plasticisers. The softening effect is therefore presumably due to changes in crosslink density. In each case, for those techniques where property differences were observed, the 'hydrolysed' sample aged in a closed system showed the greatest changes whereas the sample 'hydrolysed' open to the air showed no significant changes when compared to those of the virgin rubber.

GC-MS analysis of the toluene extractable fraction from all the samples aged in a closed system (including the 'hydrolysed' material) showed the presence of 2-ethylhexanoic acid. The extractable matter from the open air-aged sample showed little evidence of 2-ethylhexanoic acid suggesting loss from volatilisation in this case. Interestingly, there was no evidence of residual catalyst within the extractable matter suggesting it may be associated in some way to the rubber network.

Overall, the results suggest a common degradation mechanism for all the samples aged in a closed system (including the 'hydrolysed' material). This ageing mechanism is possibly acid accelerated hydrolysis (via hydronium ions) of the siloxane network as indicated by the presence of 2-ethylhexanoic acid.

**“Use of Pyrolysis GC-MS to Assess the Thermal Degradation Behaviour of Polymers
Containing Chlorine”**

I.M.Horn and A.R.Skinner (AWE)

N.Dadvand, R.S.Lehrle, I.W.Parsons and M.Rollinson (Birmingham University, UK)

AWE has commissioned a study by Birmingham University to assess the thermal degradation of a loaded rubber consisting of a mixture of neoprene and chlorobutyl rubbers by pyrolysis GC-MS. Details of the pyrolysis technique and subsequent data analysis are provided. This preliminary study has shown evidence of the production of hydrogen chloride by the chlorobutyl rubber constituent at low pyrolysis temperatures (100 °C) and the loaded rubber material at higher temperatures. These observations suggest the presence of a thermal dehydrohalogenation method at temperatures approaching the system environment.

“Measurement of Volatile Evolution Induced by Exposure to Simulated α Radiation”

J. Murphy, M. Patel (AWE)

S. Powell and P. Smith (LANL)

Irradiation of polymer samples using an accelerated beam of He^{2+} ions passed through a 10mm thick window of havar foil has been performed. Such an irradiation simulates the effects of large a radiation doses, on a vastly reduced time-scale. The experimental set up was designed so that the irradiated materials were contained within a small sample chamber (approx. 1cc). This was isolated from the main vacuum chamber of the ion beam by means of the foil window. A mass spectrometer linked directly to the sample chamber facilitated analysis of gaseous products given of by the materials as a consequence of irradiation. Samples of a poly(urethane) formulation based upon MDI and a low molecular weight poly(ester) showed an increase in the rate of outgassing at relatively low radiation doses. Only when exposure was performed at high dose rates to yield extremely high doses were any new low molecular weight species evident in the mass spectra. Samples of a polymer formulation based upon poly(vinyl acetate) and poly(vinyl alcohol) again indicated an increase in the rate of outgassing. However, at relatively low doses, changes were evident in the mass spectra indicating radiation induced volatile production from the material.